

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 424 380 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
02.06.2004 Bulletin 2004/23

(51) Int Cl.⁷: **C09K 7/06, C08G 69/26**

(21) Application number: **03394107.1**

(22) Date of filing: **18.11.2003**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(30) Priority: **25.11.2002 US 303037**

(71) Applicant: **Elementis Specialties, Inc.**
Hightstown, New Jersey 08520 (US)

(72) Inventors:
• **Thompson, Jeffrey**
Hightstown New Jersey 08520 (US)

- **Dino, David**
Cranbury New Jersey 08512 (US)
- **Jobbins, Richard**
Freehold New Jersey 07728 (US)
- **Matyi, Mark, Jr.**
North Hanover New Jersey 08562 (US)

(74) Representative: **Duffy, Assumpta Dympna et al**
F. R. Kelly & Co.,
27 Clyde Road,
Ballsbridge
Dublin 4 (IE)

(54) **Compositions for drilling fluids useful to provide flat temperature rheology to such fluids over a wide temperature range and drilling fluids containing such compositions**

(57) The invention is of oil-based drilling fluids including invert emulsion fluids that are able to maintain a relatively consistent rheological profile over a wide temperature range. The invention also includes new additives that enable the preparation of drilling fluids with viscosities that are less affected by temperature over a temperature range from less than about 40°F to more than about 250°F compared to conventional fluids.

These additives are based on reaction products of polyamines and carboxylic acids with two or more carboxylic moieties combined with alkoxyated amines and fatty acid amides. In addition, this invention permits the use of reduced amounts of organoclay rheological additives in drilling fluids.

EP 1 424 380 A1

Description

FIELD OF THE INVENTION

5 [0001] This invention relates to compositions suitable for use as additives for drilling fluids, and to drilling fluids comprising said compositions having improved rheological properties. The invention also relates to additives that provide rheological properties to drilling fluids relatively independent of the varying temperatures encountered in oil well drilling operations at various depths, particularly in deep water drilling.

10 BACKGROUND OF THE INVENTION

[0002] Drilling fluids have been used since the very beginning of oil well drilling operations in the United States and drilling fluids and their chemistry have been and remain an important area for scientific and chemical investigations. The use and desired properties of drilling fluids are comprehensively reviewed in recent U.S. Patent Nos. 6,339,048 and 6,462,096, issued to the assignee of this application, the entire disclosures of which are incorporated herein by reference.

15 [0003] A drilling fluid is a thixotropic system and exhibits low viscosity when sheared during cutting of the hole into the ground, during agitation and circulation but, when such shearing action is halted, must quickly thicken to among other things hold the "cuttings" from the drill hole in place without sinking. The fluid must therefore become thick rapidly, reaching sufficient gel strength before such suspended materials fall any significant distance. Importantly, this behavior must be totally reversible at all temperatures encountered in the borehole. In addition, even when the drilling fluid is free flowing, it must retain a sufficiently high viscosity to carry all cuttings and other particulate matter from the bottom of the hole back up to the surface.

20 [0004] Since the end of the second World War, hydrocarbon drilling for exploratory and production wells has increasingly been done from platforms located in water settings, often called off-shore drilling. Such fresh and salt water drilling employs floating barges and rigs often fixed in some fashion to the submerged surface of the earth.

[0005] Economic and technical advances have recently pushed these drilling operations into deeper waters. Although advances in equipment and engineering have yielded technology capable of drilling in water depths up to 10,000 feet or more, advances required in drilling fluid technology have lagged.

30 [0006] A major problem with oil-based drilling fluids in deepwater drilling is rheological additive temperature sensitivity over the temperature range encountered. During circulation, the drilling fluid typically reaches bottom hole temperatures of about 60 to 80°C followed by cooling to lower than 5°C in the riser during its travel upward (due to the inherent low temperature of sea water far below the ocean surface). For successful deepwater drilling, the mud needs to simultaneously suspend the solids and remain pumpable with proper viscosity over these wide temperature ranges.

35 [0007] Drilling fluids thickened with conventional organophilic clay rheological additives particularly suffer considerable viscosity build as the drilling fluid is cooled from a temperature of 60 to 5°C, for example. As a result of this viscosity increase, the drilling fluid, when it reaches low temperatures, is more difficult to pump, the equivalent circulating density (ECD) is increased and losses to the formation (lost circulation) frequently increase.

40 [0008] The requirements for drilling fluids with enhanced temperature properties have also become more complex over the past two decades as a result of changes in directional drilling technology, in which a well is drilled at an angle other than vertical. Such wells are widely known as deviated wells.

[0009] Methods for drilling deviating wells have changed greatly over recent years with the production of more powerful and reliable downhole motors, and the invention of more accurate methods utilizing wireline techniques as well as the highly computerized downhole, sensing and micro reduction equipment, including improvements in sounding apparatus and microwave transmission. These techniques permit the instantaneous acquisition of data relating to down-hole conditions without the need to remove the drill string and in fact mean that holes can, and are, drilled at ever increasing lengths.

50 [0010] The advantages of directional drilling include (1) directional drilling allows tapping of fields which cannot effectively be reached by vertical drilling; (2) such drilling permits the use of more economical land-based equipment to explore the immediate off-shore environment; and (3) such drilling make possible the drilling of multiple wells up to several miles from one another, sharing the cost of a single site. In addition, in certain geological formations, increased production can be achieved by deviating the well off-vertical so as to facilitate perforation and development of a narrow producing zone, or redevelopment of a depleted formation.

55 [0011] Use of a downhole motor allows the hole to be deviated by the introduction of a fixed offset or bend just above the drill bit. This offset or bend can be oriented by modern MWD systems which are capable of reporting accurately the current bit and toolface hole angle and azimuth (i.e. the orientation with respect to the upper portion of the hole). It is accordingly possible to rotate the drill string until the toolface has achieved the desired direction of deviation, and then to fix the drill string in place and commence the deviation by starting the motor to extend the hole in the desired

deviated direction.

[0012] There are, however, a number of inherent problems in the use of directional drilling, which affect the requirements of a drilling mud; namely:

- 5 • As in deep water drilling, increased ranges of temperatures are encountered.
- The annulus carrying the mud to the surface is no longer vertical and extends to far greater distances versus vertical wells.
- 10 • Gravity on a horizontal hole pulls cuttings, weighting material and particulate matter, not controlled by the drilling fluid, to the bottom side of the bore (not the bottom of the hole as in traditional drilling) and results in drag on the bore wall.
- The amount of drilling mud required is increased since the distances are greater, and the time required for the mud to reach the earth's surface also increases.
- 15 • Curves and kinks in the hole's direction can accumulate cuttings and additives.

[0013] In order to obviate or mitigate these problems, which can cost oil and gas companies millions of dollars per hole, it is an object of the invention to provide drilling fluids with rheological properties particularly appropriate for directional drilling including the improved viscosity stability with temperature discussed above.

[0014] For background, it has been long known that organoclays (also called organophilic clays) can be used to thicken drilling fluids. See the very early article by the employee of the assignee hereof J. W. Jordan, "Proceedings of the 10th National Conference on Clays and Clay Minerals" (1963), which discusses a wide range of drilling applications of organoclays from high polarity liquids to low polarity liquids.

[0015] Previously mentioned U.S. Patent No. 6,462,096 discloses oil-based invert emulsion drilling fluids that provide more stable drilling fluid viscosity and anti-settling performance over varying temperatures when compared to conventional fluids containing organoclays.

[0016] Patents of the prior art that show developments related to either drilling fluids or chemistry of additives include the following:

[0017] U.S. Patent No. 3,514,399 teaches the use of a mixed dimer acid-monocarboxylic acid salt of an imidazoline in a drilling fluid.

[0018] U.S. Patent No. 5,260,268 describes a product introduced into a well borehole which encompasses water-based drilling fluids and shows a composition comprised of a polycarboxylic acrylating agent reacted with an amine-terminated polyethylene of a molecular weight average from 600 to 10,000. While ethoxylated amines are discussed as a surfactant which may be used in conjunction with the composition, there is no teaching of applications in an oil-based invert emulsion drilling fluid.

[0019] U.S. Patent Application Publication No. 2001/0009890 shows an invert emulsion suitable for drilling a subterranean well which uses an ester of a C₁ to C₁₂ alcohol and a C₈ to C₂₄ monocarboxylic acid - Ethomeen C/15 can be used as an agent in the invention described in the application.

[0020] U.S. Patent No. 5,536,871 issued to the assignee hereof describes a rheological additive which comprises the reaction product of a polyalkoxylated nitrogen-containing compound such as polyoxyethylene (5) cocoalkylamine, a polycarboxylic acid including dimer acids and a liquid diamine.

[0021] U.S. Patent No. 5,610,110 also issued to assignee hereof shows an improved drilling fluid containing a reaction product of an alkoxylated aliphatic amino compound and an organic polycarboxylic acid and a clay based organoclay.

[0022] U.S. Patent No. 5,909,779 at Col. 4, lines 55 to Col. 5, line 15 contains a large laundry list of surfactants, wetting agents and viscosifying agents conventionally used in oil-based drilling fluids including fatty acids, polyamines, imidazoline derivatives and polycarboxylic acids and soaps of fatty acids.

[0023] Recent Dow Chemical Company U.S. Patent No. 6,291,406 describes a well treatment fluid using an amine surfactant to provide a sufficiently stable emulsion. Ethomeens are discussed, particularly bis(2-hydroxyethyl) co-camines and oleyamines.

[0024] Commercial rheological drilling fluid additives presently available on the market, however, tend to have increased viscosity while the fluid temperature is low, requiring increased pump pressure which in turn causes increased wear of the drilling gear. Increased pumping horsepower becomes necessary to pump drilling muds through long distances, and increased down-hole pressure under pumping conditions increases fluid loss, fracturing and damage of the formation. Prior art methods of reducing drilling fluid viscosity are not satisfactory because the resultant drilling fluids fail to maintain adequate suspension characteristics when the fluid temperature changes, for example, at down-hole conditions.

[0025] There is clearly an unfilled need which has been growing in the past decade for drilling fluids that are able to maintain a relatively consistent rheological profile over a wide temperature range; it is believed that the below unexpected described invention fills this need.

SUMMARY OF THE INVENTION

[0026] The invention herein covers new additives that enable the preparation of drilling fluids with viscosities that are less affected by temperature over a temperature range from less than about 40°F to more than about 250°F compared to conventional fluids. In addition, this invention permits the use of reduced amounts of organoclay rheological additives with the attendant reduction in cost. In fact, in some cases organoclays can be completely eliminated.

[0027] According to one aspect, this invention provides a mixture composition comprising as the first ingredient the reaction product of a di-, tri- or polyamine with an acid containing at least two carboxyl functional groups to form a polyamide and as the second mixture ingredient an alkoxyated alkylamine. The alkoxyated amine can be added to the polyamide before, during, or after its synthesis or added directly to the drilling mud as a separate component.

[0028] According to another aspect, this invention provides a mixture composition comprising the reaction product of a di-, tri- or polyamine with an acid containing at least two carboxyl functional groups to form a polyamide and as the second ingredient either (a) a fatty acid amide or (b) a mixture of a fatty acid amide and alkoxyated alkylamine which can be added to the polyamide before, during or after its synthesis or added to the drilling mud as a separate component.

[0029] In yet another aspect, this invention provides a reaction product comprising a di-, tri- or polyamine, an acid containing at least two carboxyl functional groups and an alkoxyated alkylamine. A fatty acid amide may optionally be added to this reaction product before, during or after its synthesis or added to the drilling mud as a separate component.

[0030] In another aspect, this invention provides a reaction product comprising a di-, tri-, or polyamine, an acid containing at least two carboxyl functional groups, an alkoxyated alkylamine and a fatty acid amide. The fatty acid amide can be added prior, during or after the reaction or added directly to the drilling mud as a separate component.

[0031] A further embodiment of the invention provides for a drilling fluid composition comprising an oil-based mud in which the above inventive reaction products are present individually or in combination.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] Fig. 1 and Fig. 2 show that when an additive made according to this invention is added to an oil-based drilling mud, the viscosity as expressed by a Fann viscometer dial reading is much less temperature dependent than when organoclays are used alone. It is also evident that the combination of 2 ppb of BENTONE® 155 with 0.5 ppb of the invention has a similar viscosity to 4 ppb of the organoclay at 180°F and 2 ppb of the clay at 40°F. The value of this phenomenon will be obvious to one skilled in the art.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0033] The invention provides compositions that reduce the effects of temperature on the viscosity of an invert emulsion drilling fluid. The viscosity vs. temperature profile is maintained more uniformly from less than about 40°F to greater than about 250°F for extended periods of time. When used in combination with organophilic clay, the invention maintains characteristics associated with organophilic clays in oil and synthetic based drilling fluids.

[0034] Additionally, the additive has strong value in deep-water drilling. Among the main positive attributes are the reduced high and low shear viscosity at sub-ambient temperatures as compared to a drilling mud exhibiting similar rheological properties at ambient temperature with just organoclay alone as the rheological agent. This reduced viscosity at low temperature leads to a greater ability to control formation pressure while minimizing the risk of lost returns.

[0035] The term "drilling fluid" conventionally denotes any of a number of liquid and gaseous fluids and mixtures of fluids and solids (as solid suspensions, mixtures and emulsions of liquids, gases and solids) used in operations to drill boreholes into the earth. It is synonymous with "drilling mud" in general usage.

[0036] This invention particularly covers generally petroleum or synthetic oil-based drilling fluids we call oil based drilling fluids. More particularly, it relates to an oil based drilling fluid often referred to as an invert emulsion drilling fluid, which is a water in oil emulsion whose continuous phase is oil. The water phase, or internal phase, is typically a brine for example 25% calcium chloride. This water or brine phase can range from 0% in all oil muds to in excess of 50% in invert emulsion drilling fluids.

[0037] An important embodiment of this invention relates to a drilling fluid containing a composition which is a mixture or blend of (1) a reaction product of a specific polyamine and a carboxylic acid with at least two carboxylic moieties and (2) an alkoxyated amine. The use of this unique mixture as an additive for an invert emulsion drilling fluid surprisingly improves the fluid's rheological properties. The resultant drilling fluids have a relatively constant viscosity over a

wide temperature range. More surprisingly, the viscosity of the drilling fluid of the invention is relatively low at reduced temperatures while providing sufficient viscosity under downhole temperatures to reduce barite sag and suspend drill cuttings.

[0038] The additive comprises the following. First discussed are the components of the reaction product and its production.

Fatty Acids

[0039] Any carboxylic acid with at least two carboxylic moieties can be used for producing the reaction product component of the present invention. Dimer acids are preferred; dimer acids of C₁₆ and C₁₈ fatty acid are particularly preferred. Such dimer acids can be fully hydrogenated, partially hydrogenated, or not hydrogenated at all. Useful dimer acids also include products resulting from the dimerization of C₁₆ to C₁₈ unsaturated fatty acids.

[0040] Generally when used, the dimer acids preferably have an average from about 18, preferably from about 28 to about 48 and more preferably to about 40 carbon atoms. Most preferably dimer acids have 36 carbon atoms.

[0041] Useful dimer acids are preferably prepared from C₁₈ fatty acids, such as oleic acids. Useful dimer acids are described in U.S. Pat. Nos. 2,482,760, 2,482,761, 2,731,481, 2,793,219, 2,964,545, 2,978,4681, 3,157,681, and 3,256,304, the entire disclosures of which are incorporated herein by reference.

[0042] Examples of most preferred dimer acids include the Empol® product line available from Cognis, Inc., Pripol™ dimer acids available from Uniqema and HYSTRENE® dimer acids formerly available from Humko Chemical.

[0043] It is recognized that commercially available dimer fatty acids contain a mixture of monomer, dimer, and trimer acids. Preferably, in order to achieve optimal results, the dimer fatty acid used has a specific dimer acid content as increased monomer and trimer concentration hinder the additive's performance. A person of ordinary skills in the art recognizes that commercial products may be distilled or otherwise processed to ensure certain dimer content. Preferably, suitable dimer acid has a dimer content of at least 80%, more preferably above 90%.

[0044] Empol® 1061 with a dimer acid content of 92 - 96% is the preferred dimer acid for the present invention.

Polyamines

[0045] Polyamines having an amine functionality of two or more are used for the preparation of the reaction product of the present invention. Most preferably, polyamines from the family of polyethylene polyamines having a amine functionality of two or more should be used.

[0046] Di-, tri-, and polyamines and their combinations are most suitable for use in this invention. Representative such amines include ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine and other members of this series. Branched polyamines and polyamines made with different alkyl groups can be used.

[0047] Triamines are most preferable, particularly diethylenetetramine (DETA). DETA has been assigned a CAS No. of 111-40-0. It is commercially available from Huntsman International.

Making the Reaction Product

[0048] Specifics on processing of polyamines and carboxylic acids are well known and can be used in making the reaction product of this invention. Preferably, the molar ratio between the amine functional group and carboxyl functional group is between 4:1 and 1:1. The preferred range is from 1.5:1.0 to 3:1, most preferably about 2:1. For example, mixtures of more than one dimer acid and/or more than one polyamine can be used. A representative manufacturing process is illustrated in the examples following hereafter. It should be noted that these reactions may generate imidazolines and other side products.

Alkoxyated Amines

[0049] Important to this invention in an important embodiment is that a suitable alkoxyated alkyl amine is mixed into or blended into the reaction product produced by the reaction of the carboxylic acid with the polyamine as described above or is otherwise added directly to the drilling mud.

[0050] Many alkyl alkoxyated amines are suitable for the present invention.

[0051] Any alkoxyated amine or similarly derivitized amines may be used. Suitable alkoxyated amines include amines of various degrees of alkoxylation. Representative useful chemicals include the entire Ethomeen®, Propomeen® and the Ethoduomeen® product lines of Akzo Nobel.

[0052] Preferred are amines with up to about 50 units of alkoxylation per molecule (e.g. Ethomeen® 18/60). More preferred are amines with up to about 15-25 units of alkoxylation (e.g. Ethomeen® C/25, T/25, S/25, 18/25; Ethoduomeen® T/25). Most preferred are amines with up to about 10 units of alkoxylation (e.g. Propomeen® C/12, O/12, T/

12; Ethoduomeen® T/13, T/20; Ethomeen® C/12, C/15, C/20, O/12, O/15, T/12, T/15, S/12, S/15, S/20, 18/12, 18/15 and 18/20).

[0053] The most preferred amines are polyoxyethylene (5) cocoalkylamines, available, for example, under the trade-name Ethomeen® C/15 from Akzo Nobel (New Brunswick, NJ). Ethomeen® C/15 has a general formula of

$RN[(CH_2CH_2O)_m(CH_2CH_2O)_nH]$ wherein R is cocoalkyl, and $m+n=5$.

[0054] Optionally, the alkoxyated amine may be added prior to the reaction between the dimer acid and polyamines, or blended after the reaction step. If added prior to the reaction or at the reaction temperature, some esters may be formed between the dimer acid carboxyls and the alkoxyated amine hydroxyls.

[0055] In a preferred embodiment, the two components are mixed or blended in a weight ratio range of 95:5 to 5:95.

The preferred ratio range is 80:20 to 30:70 and the most preferred ratio is 55:45 reaction product to alkoxyated amine.

Fatty Acid Amides

[0056] Optionally, additional ingredients such as fatty acid amides and related alkoxyated derivatives can be blended into or reacted with the polyamide reaction product.

[0057] Suitable fatty acid amides, such as the Aramid® product line by Akzo Nobel includes high temperature melting amides of fatty acids that are sparingly soluble in drilling muds. Additionally, alkoxyated fatty acid amides, such as the Ethomid® product line by Akzo Nobel can be used.

[0058] While the above is the preferred formulation, other compositions of varying molar ratios of raw materials can be used. Additionally, alternate commercial dimer fatty acids can be reacted with various amines to generate the reaction polymer. It however should also be noted that the alkoxyated amine could be reacted with the dimer acid/diethylenetriamine polymer generating compositions which can be further modified by blending amine derivatives (e. g. fatty acid amides) and this is intended to be included in this invention.

Preparation of the Drilling Fluids

[0059] The compositions of this invention described above will be used primarily as an additive to oil-based drilling fluids and most particularly for oil-based invert emulsion drilling fluids employed in a variety of drilling applications. The term oil-based drilling fluid is defined as a drilling fluid in which the continuous phase is hydrocarbon based. Oil-based fluids formulated with over 5% water or brine are classified as oil-based invert emulsion drilling fluids. Commonly, oil-based invert emulsion drilling fluids will contain water or brine as the discontinuous phase in any proportion up to about 50%.

[0060] A process for preparing invert emulsion drilling fluids (oil muds) involves using a mixing device to incorporate the individual components making up that fluid. Primary and secondary emulsifiers and wetting agents (surfactant mix) are added to the base oil (continuous phase) under moderate agitation. The water phase, typically a brine, is added to the base oil/surfactant mix along with alkalinity control agents and acid gas scavengers. Rheological additives as well as fluid loss control materials, weighting agents and corrosion inhibition chemicals may also be included, and the agitation is continued to ensure dispersion of each ingredient and homogenize the resulting fluidized mixture.

Suitable Oil Base

[0061] Diesel oil, mineral oil, synthetic oil, vegetable oil, fish oil, paraffinics, and/or ester-based oils can all be used as single components or as blends.

Suitable Brine Content

[0062] Water in the form of brine is often used in forming the internal phase of these type fluids. Water can be defined as an aqueous solution which can contain from about 10 to 350,000 parts-per-million of metal salts such as lithium, sodium, potassium, magnesium, cesium, or calcium salts. The preferred brines used to form the internal phase of the preferred fluid of the invention can also contain from about 5 to about 35% by weight calcium chloride and may contain various amounts of other dissolved salts such as sodium bicarbonate, sodium sulfate, sodium acetate, sodium borate, potassium chloride, sodium chloride or formates (sodium, calcium, or cesium).

[0063] The ratio of water (brine) to oil in the emulsions of the invention should generally provide as high a brine content as possible while still maintaining a stable emulsion. Oil/brine ratios in the range from about 97:3 to about 50:50 have been found to work satisfactorily, depending upon the particular oil and mud weight. Thus the water content of a typical drilling fluid prepared according to the teachings of the invention will have an aqueous (water) content of about 0 to 50 volume percent.

Suitable Emulsifiers

[0064] In order to form a more stable emulsion, an emulsifier can also be added to the external, the internal or both phases of the drilling fluid. The emulsifier is preferably selected from a number of organic acids which are familiar to those skilled in the drilling fluid area, including the monocarboxyl alkanolic, alkenolic, or alkynolic fatty acids containing from 3 to 20 carbon atoms, and mixtures thereof. Examples of this group of acids include stearic, oleic, caproic, capric and butyric acids. Adipic acid, a member of the aliphatic dicarboxylic acids can also be used. More preferred surfactants or emulsifiers include fatty acid calcium salts and lecithin. Most preferred surfactants or emulsifiers include oxidized tall oil, polyaminated fatty acids, and partial amides of fatty acids.

[0065] An important class of heterocyclic additives which we believe assist in regulating the flow properties of the drilling muds according to the invention are the imidazoline compounds. Other important members of this heterocyclic group are alkyipyridines.

[0066] Industrially obtainable amine compounds for use as emulsifiers are often derived from the epoxidation of olefinically unsaturated hydrocarbon compounds with subsequent introduction of the N function by addition to the epoxide group. The reaction of the epoxidized intermediate components with primary or secondary amines to form the corresponding alkanolamines is of significance in this regard. Polyamines, particularly lower polyamines of the corresponding alkylenediamine type, are also suitable for opening of the epoxide ring.

[0067] Another class of the oleophilic amine compounds useful as emulsifiers are aminoamides derived from preferably long-chain carboxylic acids and polyfunctional, particularly lower, amines of the above-mentioned type. The key factor in their case is that at least one of the amino functions is not bound in amide form, but remains intact as a potentially salt-forming basic amino group. The basic amino groups, where they are formed as secondary or tertiary amino groups, may contain hydroxyalkyl substituents and, in particular, lower hydroxyalkyl substituents containing up to 5 and preferably up to 3 C atoms in addition to the oleophilic part of the molecule.

[0068] Suitable N-basic starting components for the preparation of such adducts containing long-chain oleophilic molecule constituents are monoethanolamine or diethanolamine.

[0069] **Weighting materials** are also often used to weight the well bore fluids of the invention to a density in the preferred range from about 8 to 18 pounds per gallon and greater. Weighting materials well known in the art include barite, ilmenite, calcium carbonate, iron oxide and lead sulfide. The preferred weighting material is commercially available barite.

[0070] **Organophilic Clays.** Organoclays made from bentonite, hectorite and attapulgite clays can be added to the inventive drilling fluids. There are a large number of suppliers of such clays in addition to Elementis Specialties' BENTONE® product line including Rockwood Specialties, Inc. and Sud Chemie GmbH. Although organoclay can be a useful component, it is not a necessary component of the drilling fluid.

Blending Process

[0071] Drilling fluids preparations preferably contain between ¼ and 15 pounds of the inventive mixture per barrel of fluids, more preferred concentration is ¼ to 10 pounds-per-barrel and most preferably ¼ to 5 pounds-per-barrel.

[0072] As shown above, a skilled artisan will readily recognize that additional additives: weighting agents, emulsifiers, wetting agents, viscosifiers, fluid loss control agents, and other agents can be used with this invention. A number of other additives besides rheological additives regulating viscosity and anti-settling properties, providing other properties, can also be used in the fluid so as to obtain desired application properties, such as, for example, anti-settling agents and fluid loss-prevention additives.

[0073] The drilling fluids of the present invention generally have a lower viscosity at 40°F than conventional muds formulated with sufficient organoclay to provide suspension at bottom hole temperatures. When used in drilling operations, the present drilling fluids allow the use of a lower pumping power to pump drilling muds through long distances, thereby reducing down-hole pressures. Consequently, fluid loss, fracturing and damage of the formation are all minimized. Drilling fluids of the present invention also advantageously maintain the suspension characteristics typical of higher levels of organoclays at higher temperatures. The present invention is particularly useful in deep water drilling when the mud is cooled in the riser. A mud using the described invention will maintain a reduced viscosity increase in the riser when compared to drilling fluids containing conventional rheological additives.

EXAMPLES**Example 1: Preparation of the Polyamide Reaction Product**

[0074] Empol® 1061 (792.9 grams) was placed in a 2 liter, 4-neck, preweighed reactor equipped with a Barrett distilling receiver and a Friedrichs condenser. The Empol® 1061 was heated to 100°C and then diethylenetriamine

EP 1 424 380 A1

(190.6 grams) was added. The contents were heated to 240°C under a nitrogen blanket while mixing at 300 RPM. A reaction occurred with the liberation of water, which was condensed in a receiver. The reaction was allowed to continue until the acid value was ≤ 2.0 (mg KOH/gram). The reaction was halted and the reactor reweighed. A sample was taken, labeled Sample A, and given a lot number for further studies.

Example 2: Preparation of Inventive Mixture Using the Product of Example 1

[0075] Sample A was allowed to cool to 80°C under agitation. Ethomeen® C/15 (821.8 grams) was added slowly while mixing at 500 RPM. The composition was mixed for 15 minutes. All of the Ethomeen® C/15 was incorporated into the mixture. The resulting product was poured into an appropriate storage container.

Example 3: Preparation Of Reaction Product 2:

[0076] Empol® 1008 (635.2 grams) and Ethomeen® C/15 (692.1 gram) were placed in a 2 liter, 4-neck, preweighed reactor equipped with a Barrett distilling receiver and Friedrichs condenser. The contents were heated to 240°C under a nitrogen blanket while mixing at 300 rpm. The reaction was allowed to continue until the acid value was ≤ 5.0 (mg KOH/grams). Once the acid value was ≤ 5.0 , diethylenetriamine (112.6 grams) was charged to the reactor. The reaction continued for another two hours at 240°C. After this time, Armid® HT (164.0 grams) was added to the reactor and cooked for an additional 3 hours at 240°C. The resulting product was poured into storage containers.

Example 4: Preparation of Drilling Fluid and Various Tests

[0077] A typical test mud was prepared comprised of a synthetic base oil (186 grams), primary emulsifier (4 grams), secondary emulsifier (2 grams), 30% calcium chloride brine solution (75 grams) and lime (4 grams). All components were mixed together for 15 minutes. The test additive(s) was charged to the fluid and mixed for an additional 15 minutes. Barite (215 grams) was next added and the fluid mixed for another 15 minutes, total mixing time was 45 minutes. Properties of the resulting test mud were measured and evaluated.

[0078] After initial make up of all the drilling fluid (mud) and characterization was completed (120°F), the drilling fluid (mud) was subjected to a thermal treatment at 150°F for 16 hours. Drilling fluid (mud) properties were measured at 40°F, 120°F, and 180°F as per API RP 13-B standard practices.

A. Table 1 Summary

[0079]

Table 1

Drilling Fluid Formulation	
Mud Formulation	Lbs./BBL
Synthetic Based Oil	186
Primary Emulsifier	4
Secondary Emulsifier	2
30% Calcium Chloride Brine	75
Lime	4
Rheological Additive	See Tables for Concentrations
Barite	215

[0080] A drilling mud formula for the purpose of evaluating a rheological additive performance.

B. Table 2 Summary

[0081] This below table represents a Bentone® 155 concentration study in a synthetic oil-based invert emulsion drilling fluid (mud). Table 2 shows that an oil-based drilling mud incorporating organoclay alone as a rheological modifier exhibits greater than 190% high shear rate viscosity increase at 4 ppb rheological agent when the temperature is reduced from 120°F to 40°F.

EP 1 424 380 A1

[0082] The drilling mud exhibits greater than a 160% low shear rate viscosity increase at 4 ppb rheological agent when the temperature is reduced from 120°F to 40°F.

Table 2

BENTONE® 155 CONCENTRATION EVALUATION									
Rheological Additive BENTONE® 155									
Additive Concentration	2ppb			4ppb			6ppb		
OFI 800 Viscosity Test Temperature	40°F	120°F	180°F	40°F	120°F	180°F	40°F	120°F	180°F
600 RPM Reading	113	48	36	169	58	37	215	87	62
300 RPM Reading	69	30	22	110	39	25	158	59	42
200 RPM Reading	53	23	18	88	32	19	133	50	35
100 RPM Reading	36	16	12	65	24	14	99	38	26
6 RPM Reading	13	6	3	26	10	6	48	20	14
3 RPM Reading	13	5	2	25	9	6	45	18	13
Apparent Visc., cPs	57	24	18	85	29	19	108	44	31
Plastic Visc., cPs	44	18	14	59	19	12	57	38	20
Yield Point, Lbs./100 Ft ²	25	12	8	51	20	13	101	31	22

C. Table 3 Summary:

[0083]

Table 3

Impact of Example 2 on Viscosity: Temperature Profile			
Additive Concentration: BENTONE 155 (2.0 ppb)/Example 2 (1.0 ppb)			
OFI 800 Viscosity Test Temperature	40°F	120°F	180°F
600 RPM Viscosity	84	48	35
300 RPM Viscosity	50	31	24
200 RPM Viscosity	40	25	20
100 RPM Viscosity	27	19	15
6 RPM Viscosity	12	9	6
3 RPM Viscosity	11	8	5
Apparent Visc., cPs	42	24	18
Plastic Visc., cPs	34	17	11
Yield Point, Lbs./100 Ft ²	16	14	13

[0084] Table 3 presents the effect of the product of Example 2 on the viscosity of an oil-based drilling mud. When 0.5 ppb of the additive is combined with 2 ppb of BENTONE® 155, the 600 rpm Fann reading only increases by 75% (48 to 84) when the temperature is reduced from 120°F to 40°F. Two ppb of the BENTONE alone gave rise to a 135% increase (Table 2) under comparable conditions. The low shear rate viscosity, measured at 6 rpm, showed a 33.3% viscosity increase as the temperature was reduced whereas the BENTONE alone provided a 115% increase.

D. Table 4 Summary

[0085] Table 4 below presents the effects of the product of Example 3 on the viscosity of an oil-based drilling mud. When 1 ppb of the additive is used along with 3 ppb of BENTONE® 155, the 600 rpm Fann reading only increases by

56.9% (65 to 102) when the temperature is reduced from 120°F to 40°F. Four ppb of the BENTONE alone gave rise to a 190% increase. The low shear rate viscosity, measured at 6 rpm, showed a 29.4% viscosity decrease as the temperature was reduced.

Table 4

Impact of Example 3 on Viscosity: Temperature Profile			
Additive Concentration BENTONE 155 (3.0 ppb) / Example 3 (1.0 ppb)			
OFI 800 Viscosity Test Temperature	40°F	120°F	180°F
600 RPM Reading	102	65	50
300 RPM Reading	63	44	36
200 RPM Reading	48	36	30
100 RPM Reading	31	28	24
6 RPM Reading	12	17	15
3 RPM Reading	11	16	14
Apparent Visc., cPs	51	33	25
Plastic Visc., cPs	39	21	14
Yield Point, lbs./100 ft ²	24	23	22

[0086] The foregoing description and examples have been set forth merely to illustrate the invention and are not intended to be limiting. Since modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed broadly to include all variations falling within the scope of the appended claims and equivalents thereof.

Claims

1. A composition comprising:

a) the reaction product of (i) a carboxylic acid with at least two carboxylic moieties and (ii) a polyamine having an amine functionality of two or more; and

b) a chemical selected from the group consisting of (i) alkoxyated alkyl amines, (ii) fatty acid amides and (iii) mixtures thereof.

2. A composition comprising the reaction product of (a) a polyamine having an amine functionality of two or more, (b) a carboxylic acid with at least two carboxylic moieties and (c) an alkoxyated alkyl amine.

3. A composition comprising the reaction product of a) a carboxylic acid with at least two carboxylic moieties, b) a polyamine having an amine functionality of two or more, c) an alkoxyated alkyl amine and d) a fatty acid amide.

4. A composition comprising:

a) the reaction product of (i) a carboxylic acid with at least two carboxylic moieties, (ii) a polyamine having an amine functionality of two or more and (iii) an alkoxyated alkyl amine; and

b) a fatty acid amide.

5. The composition of any of Claims 1 to 4, wherein the carboxylic acid is a dimer fatty acid.

6. The composition of Claim 5, wherein the dimer fatty acid is selected from the group consisting of hydrogenated, partially hydrogenated and non-hydrogenated dimer acids with from about 20 to about 48 carbon atoms.

EP 1 424 380 A1

7. The composition of any of Claims 1 to 6, wherein the polyamine is a polyethylene polyamine.
8. The composition of Claim 7, wherein the polyamine is selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine.
9. The composition of Claim 8, wherein the polyamine is diethylenetriamine.
10. The composition of any of Claims 1 to 9, wherein the alkoxyated alkyl amine is an ethoxylated fatty amine.
11. The composition of Claim 10, wherein the ethoxylated fatty amine is an ethoxylated (5) cocoalkyl amine.
12. The composition of any of Claims 1 to 11, further comprising an organoclay.
13. An oil-based drilling fluid comprising the composition of any of Claims 1 to 12.
14. The drilling fluid of Claim 13, further comprising an organoclay.
15. The drilling fluid of Claim 13 or 14, further comprising one or more emulsifiers.

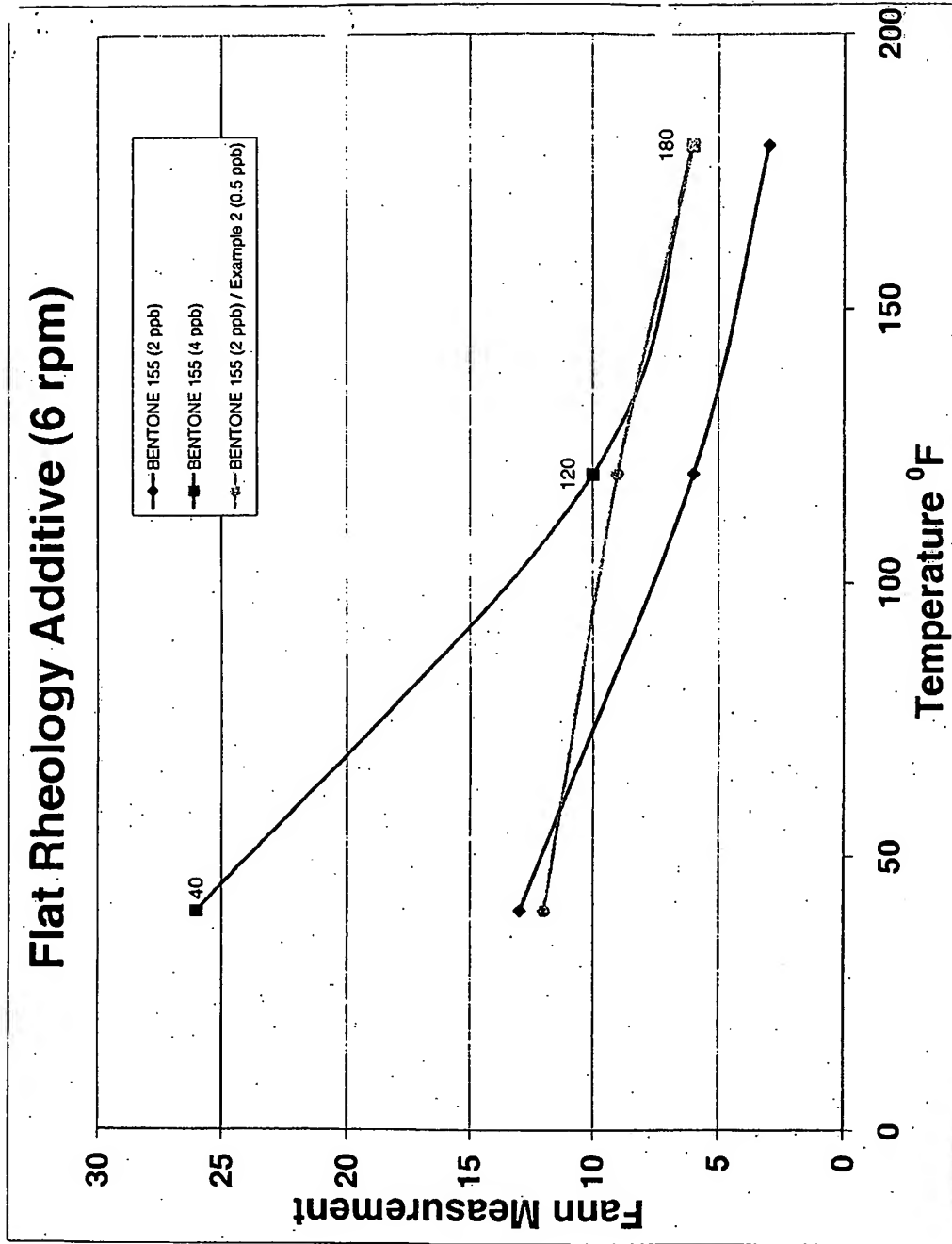


FIG. 1

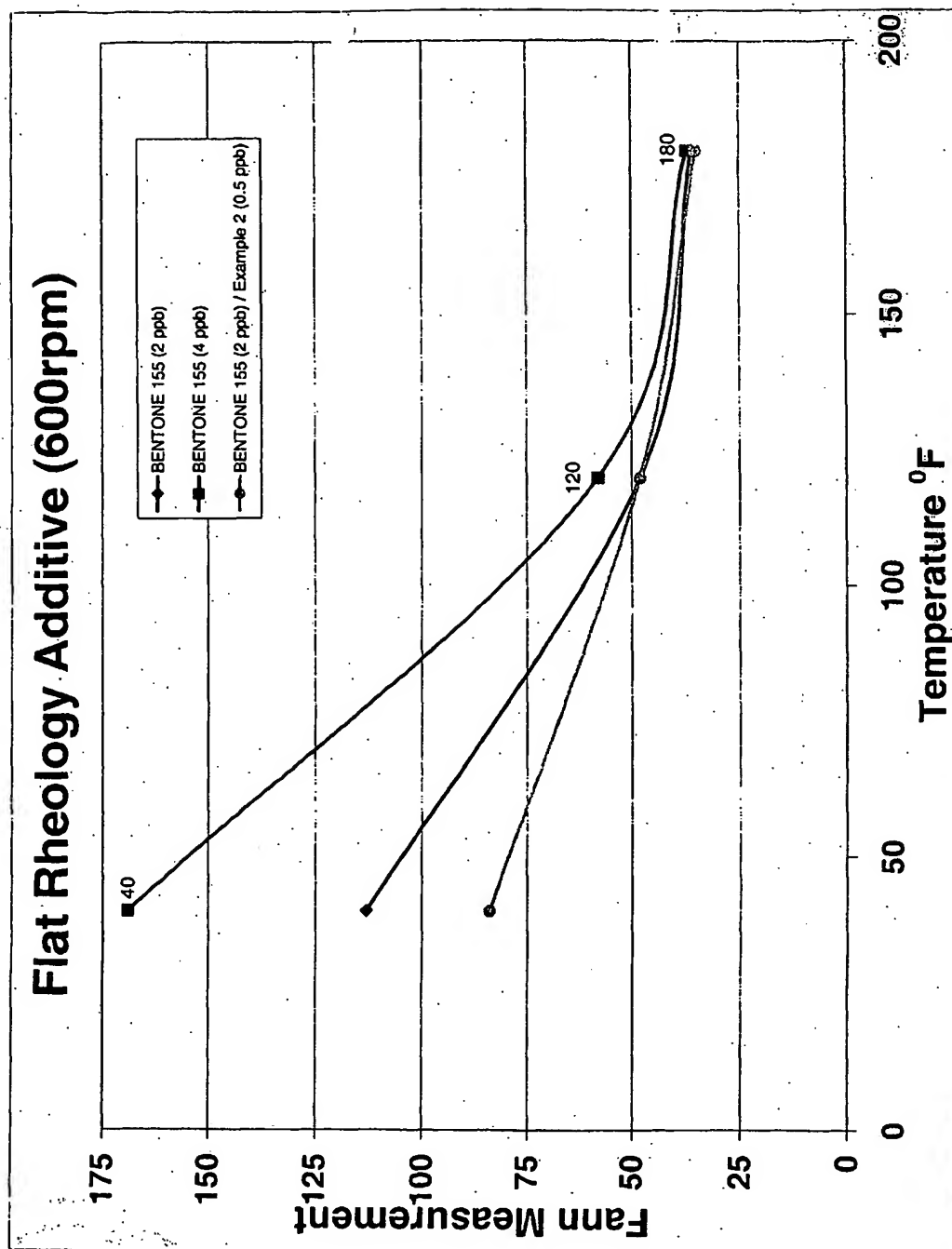


FIG. 2



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 39 4107

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 1 018 534 A (UBE INDUSTRIES) 12 July 2000 (2000-07-12) * page 3 - page 5 *	1,5	C09K7/06 C08G69/26
X	EP 0 826 750 A (RHEOX INT) 4 March 1998 (1998-03-04) * page 8 - page 9 *	2,5,6,12	
A	EP 1 111 024 A (RHEOX INC) 27 June 2001 (2001-06-27) * page 7, paragraph 52 - page 10, paragraph 70 *	1-15	
A	US 4 508 628 A (SIMPSON JAY P ET AL) 2 April 1985 (1985-04-02) * column 5 - column 6 *	1-15	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			C09K C08G C08L C09D
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 1 April 2004	Examiner Zimpfer, E
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 (03.02.2004)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 39 4107

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

01-04-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1018534 A	12-07-2000	JP 2000204240 A	25-07-2000
		JP 2000204241 A	25-07-2000
		EP 1018534 A2	12-07-2000
		US 6291633 B1	18-09-2001

EP 0826750 A	04-03-1998	US 5939475 A	17-08-1999
		CA 2212905 A1	03-03-1998
		DE 69704691 D1	07-06-2001
		DE 69704691 T2	18-04-2002
		EP 0826750 A1	04-03-1998

EP 1111024 A	27-06-2001	US 6339048 B1	15-01-2002
		CA 2322094 A1	23-06-2001
		EP 1111024 A1	27-06-2001

US 4508628 A	02-04-1985	NONE	

EPO FORM P0159

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82